



**MICROWAVE-ASSISTED
HEADSPACE IONIC LIQUID
SINGLE DROP
MICROEXTRACTION OF
CHLOROBENZENES FROM
WATER SAMPLES**

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Outline of presentation

I. Introduction

II. Microextraction

III. Microwaves

IV. Experimental

V. Results and discussion



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I. Introduction

II. Microextraction

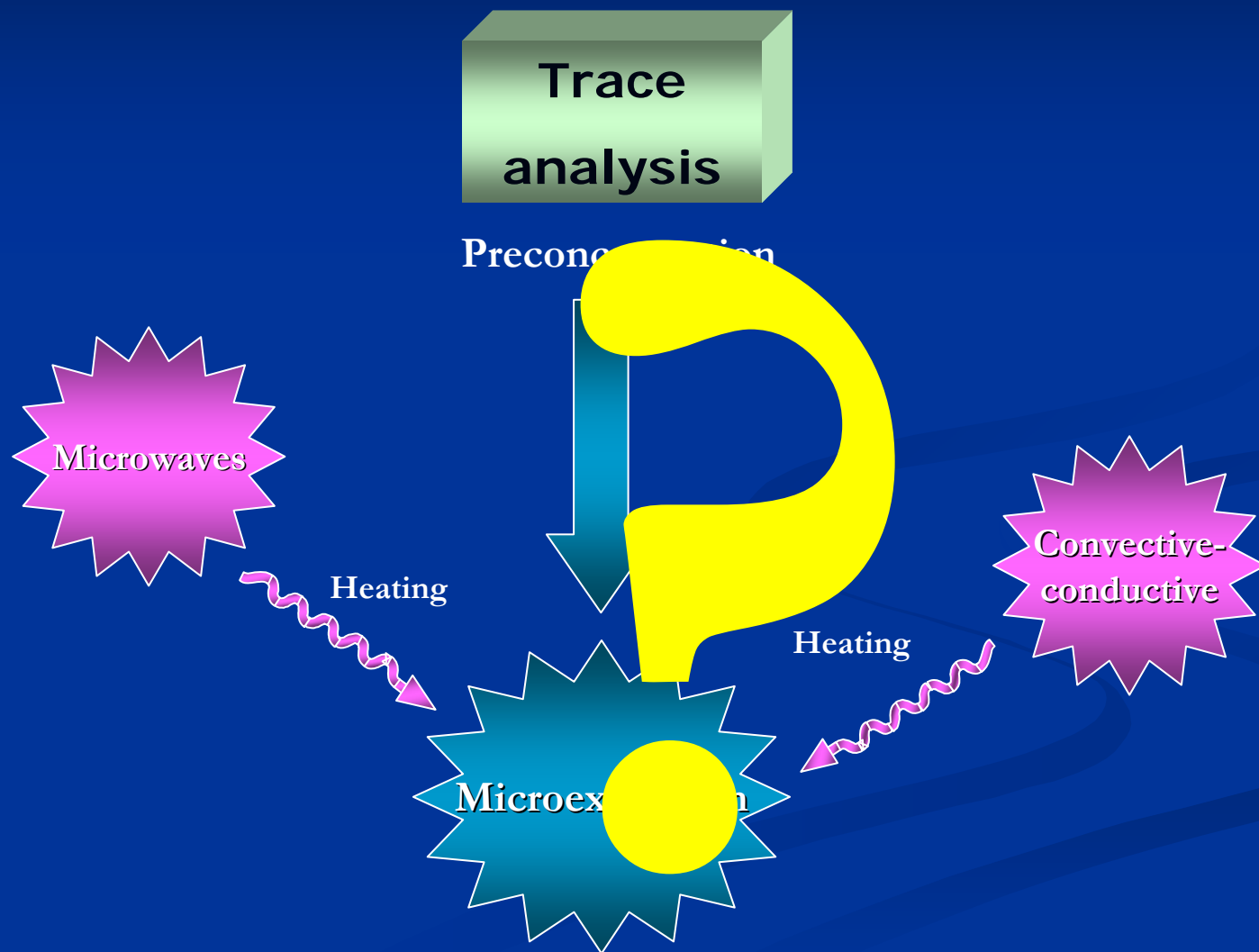
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Volatile and semivolatile analytes





Analytes

1,3-Dichlorobenzene (1,3-DCB)

1,4-Dichlorobenzene (1,4-DCB)

1,2-Dichlorobenzene (1,2-DCB)

1,3,5-Trichlorobenzene (1,3,5-TCB)

1,2,4-Trichlorobenzene (1,2,4-TCB)

1,2,3-Trichlorobenzene (1,2,3-TCB)

1,2,4,5-Tetrachlorobenzene (1,2,4,5-TeCB)

1,2,3,4-Tetrachlorobenzene (1,2,3,4-TeCB)



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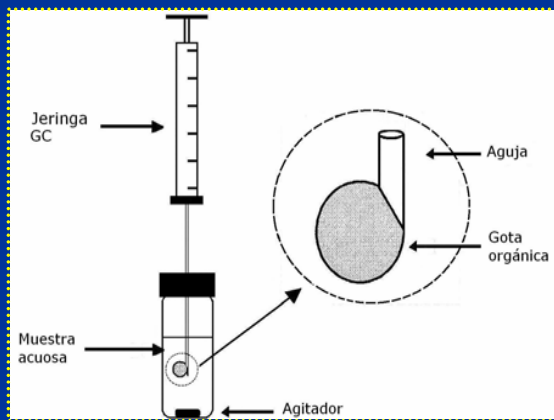
Microextraction methods

- Miniaturized extraction methods
 - ✓ Solid-phase microextraction (SPME)
 - ✓ Liquid-phase microextraction (LPME)
 - ✓ Single-drop microextraction (SDME)
- Fast
- Easy
- Economical
- High preconcentration factor
- Virtually organic solvents free

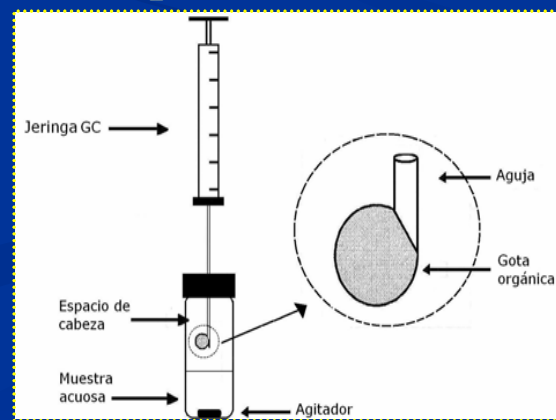
Single drop microextraction (SDME)

- Miniaturization of liquid-liquid extraction
- The extractant phase (drop) could be an organic solvent or an ionic liquid
- Modes:
 - Direct immersion (SDME)
 - Headspace (HS-SDME)

Direct immersion



Headspace





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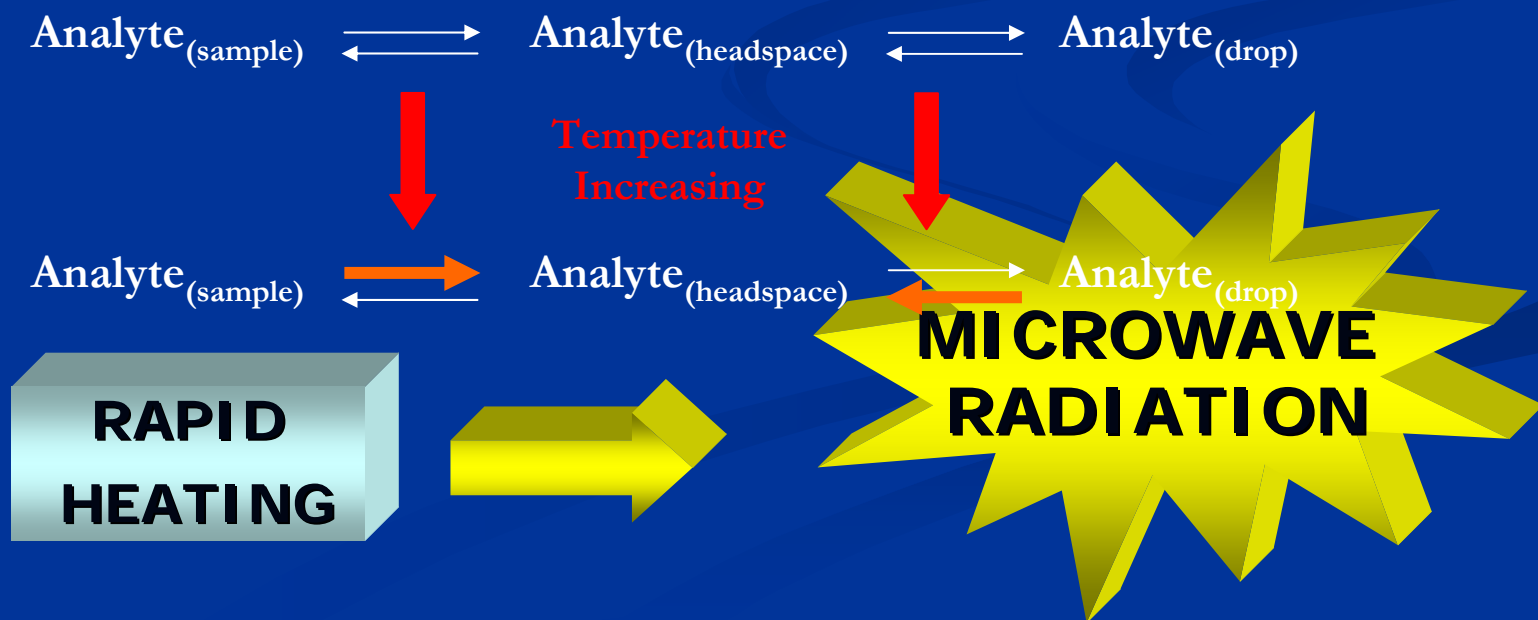
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Heating ?

- ☺ To facilitate HS-SDME, high temperatures may be required to enhance the release of analytes into the headspace.
- ☹ High-temperature extraction may also cause significant deterioration of the drop/sample distribution coefficient.





How does microwave electromagnetic radiation interact with a sample?

- ☀️ Microwaves are electromagnetic energy that can speed up the molecular movement.
- ☀️ This movement mainly occurs due to ion migration and dipole rotation.
- ☀️ The movement of molecules in a fluid is a measure of its kinetic energy.





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Instrumentation

- **Microwave oven: Domestic Samsung M1711N (2450 MHz, 800W)**
- **HPLC System: Waters multisolvent pump and Waters 996 Photodiode Array Detector (PDA) set at 210 nm (Waters, Milford, MA, USA)**
- **Column: Luna C18 (250 x 4.6 mm, 5 μ m) from Phenomenex (Torance, USA)**
- **Precolumn: Luna C18 (4 x 3 mm)**



Separation conditions

- Mobile phase: Acetonitrile-water 65:35 (v/v)
- Flow-rate: 1 mL min⁻¹

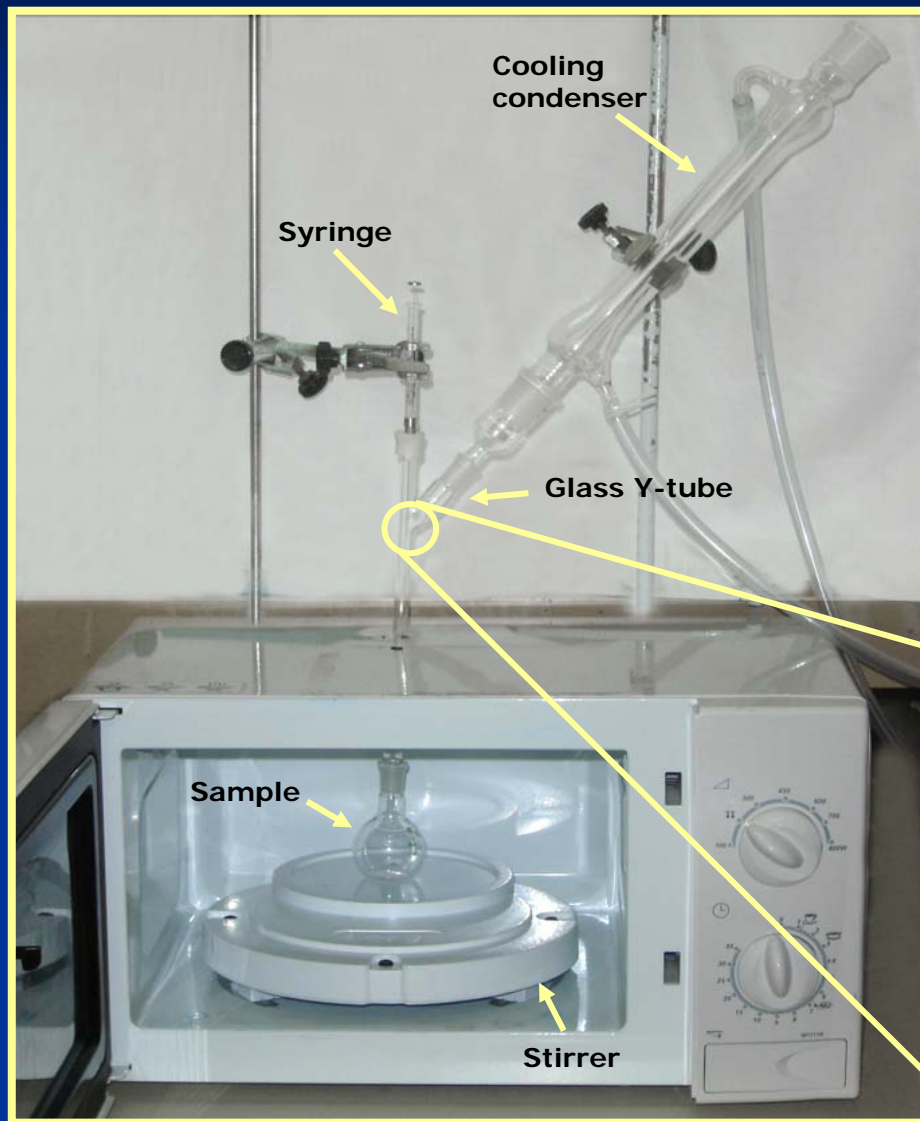
Microwave heating

- A 9-min microwave heating at 200 W and a 20-min total extraction time (i.e., heating cycles of 30 seconds) are employed.

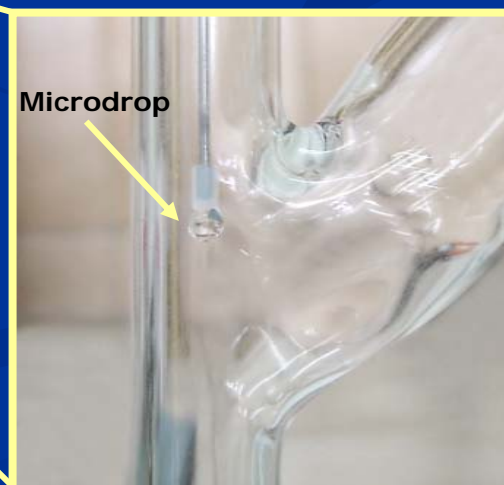




System



A 3 mm long PTFE tube is fitted to the blunt tip of a 25 μL Hamilton Gastight syringe. The microsyringe typically containing the appropriate ionic liquid is clamped above tube.





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Optimization

SCREENING

Experimental variables and levels of a Plackett-Burman design

Variable	Level	
	Low	High
Ionic strength (NaCl concentration; w/v):	0	30
Drop volume (μL)	5	8
Sample volume (mL)	10	30
Extraction time (min)	10	20
Stirring speed (rpm)	0	300
Ionic liquid type	$[\text{C}_4\text{MIM}][\text{PF}_6]$	$[\text{C}_6\text{MIM}][\text{PF}_6]$
MW power (W)	100	200
Tube length (cm)	25	34



Optimization

NON-INFLUENTIAL VARIABLES

Ionic strength (NaCl concentration; w/v): 0 %

Drop volume: 5 μL

Stirring speed: 0 rpm

MW Power: 200 W

Tube length: 25 cm

INFLUENTIAL VARIABLES

Sample volume

Extraction time

Ionic liquid type

Optimization

FACTORIAL DESIGN

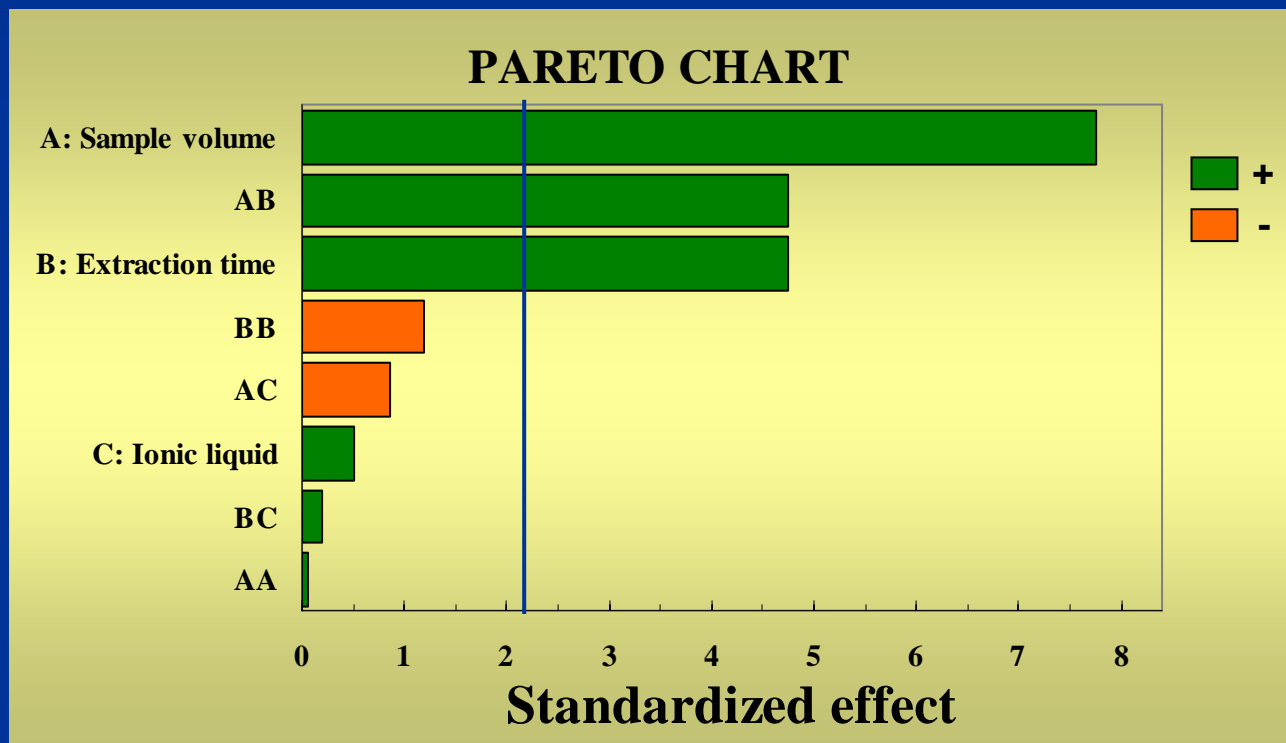
Experimental variables and levels of a Mixed-Level Factorial design

Variable	Level		
	Lower	Central	Upper
Sample volume (mL)	10	20	30
Extraction time (min)	10	15	20
Ionic liquid type	[C ₄ MIM][PF ₆]	-	[C ₆ MIM][PF ₆]



Optimization

FACTORIAL DESIGN



Optimum conditions

Ionic liquid: $[C_6MIM][PF_6]$ 1-hexyl-3-methylimidazolium hexafluorophosphate

Drop volume: 5 μ L

Extraction time: 20 minutes

Sample volume: 30 mL

Microwave power: 200 W

Glass Y-tube length: 25 cm

Stirring speed: 0 rpm

Ionic strength (NaCl concentration; w/v): 0 %



Validation

Analyte	Slope	Intercept	Correlation Coefficient (r) ^a	RSD (%) ^b	LOD ($\mu\text{g L}^{-1}$) ^c	LOQ ($\mu\text{g L}^{-1}$) ^d
1,2-DCB	0.10753 ± 0.00079	0.08 ± 0.11	0.9998	2.7	0.024	0.081
1,4-DCB	0.06688 ± 0.00052	-0.031 ± 0.072	0.9998	2.3	0.039	0.130
1,3-DCB	0.09512 ± 0.00033	-0.042 ± 0.045	0.9999	2.9	0.032	0.108
1,2,3-TCB	0.1993 ± 0.0016	-0.42 ± 0.20	0.9998	5.7	0.016	0.054
1,2,4-TCB	0.1685 ± 0.0026	0.20 ± 0.36	0.9995	5.6	0.022	0.072
1,3,5-TCB	0.2182 ± 0.0015	-0.20 ± 0.20	0.9998	3.8	0.022	0.072
1,2,3,4-TeCB	0.2684 ± 0.0017	-0.30 ± 0.22	0.9998	8.3	0.016	0.054
1,2,4,5-TeCB	0.3612 ± 0.0037	0.79 ± 0.52	0.9996	7.1	0.016	0.054

^a Linear range: 1-320 $\mu\text{g L}^{-1}$ (number of calibration points = 9).

^b Relative standard deviation (RSD); mean value for five replicate analyses; spiking level 40 $\mu\text{g L}^{-1}$.

^c Limits of detection (LODs) calculated using a S/N = 3 criterion.

^d Limits of quantification (LOQs) calculated using a S/N = 10 criterion.



Validation

Analyte	Repeatability RSD (%)		LOD ($\mu\text{g L}^{-1}$) ^c		LOQ ($\mu\text{g L}^{-1}$) ^d	
	No MW ^a	MW ^b	No MW	MW	No MW	MW
1,2-DCB	5.1	2.7	0.102	0.024	0.338	0.081
1,4-DCB	2.3	2.3	0.203	0.039	0.677	0.130
1,3-DCB	5.0	2.9	0.152	0.032	0.508	0.108
1,2,3-TCB	1.6	5.7	0.102	0.016	0.338	0.054
1,2,4-TCB	3.4	5.6	0.122	0.022	0.406	0.072
1,3,5-TCB	4.1	3.8	0.122	0.022	0.406	0.072
1,2,3,4-TeCB	3.1	8.3	0.102	0.016	0.338	0.054
1,2,4,5-TeCB	3.0	7.1	0.102	0.016	0.338	0.054

^a Relative standard deviation (RSD); mean value for five replicate analyses; spiking level $20 \mu\text{g L}^{-1}$

^b Relative standard deviation (RSD); mean value for five replicate analyses; spiking level $40 \mu\text{g L}^{-1}$.

^c Limits of detection (LODs) calculated using a $S/N = 3$ criterion.

^d Limits of quantification (LOQs) calculated using a $S/N = 10$ criterion.



Matrix effects

Analyte	Relative recoveries (%) and RSD values (%) in parentheses ^a					
	Tap water		River water		Effluent water	
	No MW	MW	No MW	MW	No MW	MW
1,2-DCB	97.3 (4.2)	96.2 (1.8)	101.1 (5.8)	100.9 (4.0)	114.1 (3.2)	88.6 (7.4)
1,4-DCB	98.0 (3.1)	91.4 (5.2)	100.5 (1.9)	98.1 (5.9)	120.6 (2.4)	83.7 (11.3)
1,3-DCB	100.9 (6.5)	96.2 (3.7)	106.6 (3.1)	99.0 (5.9)	112.1 (3.8)	82.9 (12.0)
1,2,3-TCB	96.0 (1.3)	100.1 (2.1)	101.0 (2.1)	99.7 (2.3)	86.0 (2.8)	94.9 (1.7)
1,2,4-TCB	96.5 (1.7)	103.9 (5.6)	99.3 (2.5)	101.4 (3.3)	89.5 (5.1)	90.8 (5.0)
1,3,5-TCB	94.1 (2.0)	101.3 (5.8)	101.2 (4.5)	99.7 (4.1)	83.2 (4.4)	81.7 (11.7)
1,2,3,4-TeCB	95.9 (2.8)	102.5 (4.4)	101.6 (3.9)	105.5 (6.1)	60.8 (6.6)	98.9 (4.4)
1,2,4,5-TeCB	96.8 (2.8)	101.7 (3.4)	106.1 (3.1)	100.2 (3.0)	66.0 (6.8)	93.3 (1.8)

^a Five replicate analyses at a 40 µg L⁻¹ spiking level



Conclusions

- MA-HS-IL-SDME has been developed via on-line combination of microwave heating and SDME for extraction of chlorobenzenes from water samples. The devices employed are simple in design and easily obtainable.
- The multivariate optimization strategy used allows the successful/fast determination of the optimum conditions for the main operational parameters taken into consideration during MA-HS-IL-SDME.
- The results have proven the applicability of the proposed method to analyze chlorobenzenes in water samples with the advantages of being fast, sensitive, low-cost, and freedom from use of toxic organic solvents, representing an excellent alternative to traditional and other, recently introduced, methods.



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